

BTEC 9643
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of Stephen T. Wellinghoff et al.

Serial No. 09/488,927

Filed November 24, 1999

Confirmation No. 5618

For ENERGY-ACTIVATED COMPOSITIONS FOR CONTROLLED SUSTAINED
RELEASE OF A GAS

Examiner Joseph D. Anthony

Group Art Unit: 1714

DECLARATION OF STEPHEN T. WELLINGHOFF
UNDER 37 C.F.R. §1.132TO THE COMMISSIONER OF PATENTS AND TRADEMARKS,
SIR:

I, Stephen T. Wellinghoff, hereby declare and state as follows:

1. I am a co-inventor of the subject matter claimed in the above-referenced patent application.
2. I am an Institute Scientist for the Southwest Research Institute, Division of Chemistry and Chemical Engineering. I received a B.S. in Chemistry from Case Western Reserve University in 1971, an M.S. in Macromolecular Science from the university in 1972, and a Ph.D. in Macromolecular Science from the university in 1976.
3. I have conducted extensive research in the subject matter of the present invention. I am an inventor or co-inventor of fourteen (14) United States patents directed to compositions and methods for gas generation and release. In my work, I rely not only upon my own research and experience, but also substantially on the results of research and development by others around the world published in scientific journals, as well as in the specifications of patents and published patent applications. I assess such published work by others for myself, and if I consider it to be sound and relevant, use it as a basis of knowledge and assistance in my own work.
4. I consulted with applicant's attorneys regarding the prior art references cited by the Office against the present application in the 16 September 2003 Office action. The 12

BTEC 9643
PATENT

December 2003 response filed by applicant's attorneys was based, in part, on my analysis of those references.

5. I analyzed the nine (9) references cited by the Office as anticipating the claimed subject matter including U.S. Patent No. 5,108,649 to Matsumoto, U.S. Patent No. 5,330,661 to Okuda, U.S. Patent No. 5,008,096 to Ringo, U.S. Patent No. 5,753,106 to Schenck, U.S. Patent No. 5,772,897 to Hancock, U.S. Patent No. 6,306,352 to Yoshida, U.S. Patent No. 5,783,105 to Zhang, U.S. Patent No. 5,896,126 to Yoshida and U.S. Patent No. 5,411,643 to Cawfield. It is my opinion that the claims are novel over each of those references. In addition, it is my opinion that it would not have been obvious to modify the teaching of U.S. '126 to arrive at the claimed subject matter.

6. U.S. Patent No. 5,108,649 to Matsumoto teaches a preserving agent, method and container for maintaining the freshness of fresh marine products. The preserving agent in Matsumoto Example 2 is comprised of sodium chlorite (or chlorate), iron powder and ferric oxide. While Matsumoto describes deoxidizing marine products using the preserving agent, it does not describe the generation and release of an oxidizing gas as required in the present claims. In fact, Matsumoto teaches the opposite; the preserving agent functions by reducing gas (oxygen) concentration. Matsumoto teaches the use of oxidizing agents such as chlorite, chlorate and hypochlorite for the oxidation of iron metal to oxides of iron. In the absence of oxychloro anions, finely divided iron would react with oxygen in the atmosphere to produce iron oxide by the following reaction (<http://en.wikipedia.org/wiki/Electrochemistry> - see below).

"Iron corrosion"

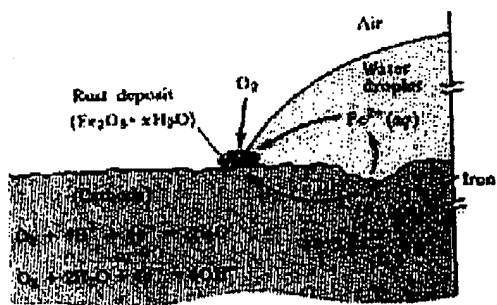


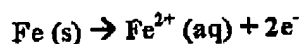
Diagram showing a water droplet over an iron surface.

BTEC 9643
PATENT

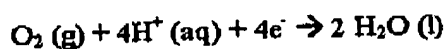
Electrochemical mechanisms are involved in iron rusting processes. For iron rust to occur, the metal has to be in contact with oxygen and water. Although chemical reactions for this process are some complex and not all of them have been completely understood, it is believed the mechanism is as follows:

Electron transferring (Reduction-Oxidation)

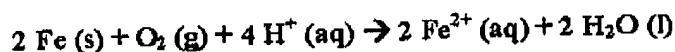
1. One surface of the metal acts as the anode where the oxidation occurs.



2. Electrons are transferred from iron reducing oxygen in the atmosphere into water on the cathode, which is placed in another region of the metal.



3. Global reaction for the process:

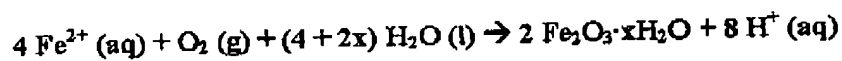


4. Standard emf for iron rusting:

$$E^{\circ} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E^{\circ} = 1.23\text{V} - (-0.44\text{V}) = 1.67\text{V}$$

Iron corrosion takes place on acid medium; H^{+} ions come from reaction between carbon dioxide in the atmosphere and water, forming carbonic acid. Fe^{2+} ions form oxides according to the following equation:



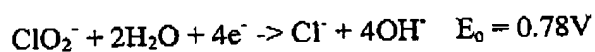
Hydrated iron (III) oxide is known as rust. Water associated with iron oxide varies, thus chemical representation is presented as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The electric circuit works as passage of electrons and ions occurs, thus if an electrolyte is present it will facilitate oxidation. That explains why rusting is quicker in salt water."

Oxidation of iron metal, first to Fe^{+2} and then secondly to Fe^{+3} (Fe_2O_3), generates no net protons since 2 protons/mole Fe are required in the first reaction and 2 protons/ Fe^{+2} are generated in the second reaction.

BTEC 9643
PATENT

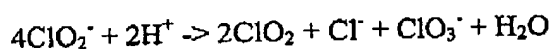
Unfortunately, this reaction alone is quite slow under normal conditions and would be unable to remove oxygen from the environment at sufficient rate for the Matsumoto application. Therefore Matsumoto adds another oxidizer, an oxychloro anion, which presumably acts as an accelerant for the corrosion reaction while not oxidizing enough iron itself to significantly deplete the iron metal-oxygen sink.

The standard redox reaction for chlorite is shown below¹:



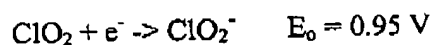
This reaction is sufficiently positive on the standard hydrogen electrode scale (SHE) to oxidize both Fe^{+2} and Fe^0 so, in principle, chlorite could either accelerate the corrosion of the metal or promote the formation of iron oxide-hydrated in situ. Conceivably, the accelerated formation of oxyhydroxide could promote air oxidation of the iron (and thus deoxygenation of the surrounding atmosphere). However, Matsumoto proposes no mechanism promoted by the presence of oxychloro anions.

Chlorine dioxide can be generated through the disproportionation reaction:



However, as can be seen from the above discussion, the oxygen reaction with iron generates no net pH change while disproportionation of chlorite to chloride and chlorate requires acidic conditions. *In addition, reduction of chlorite through oxidation of the metal would reduce acidity along with generating chloride ion.* This implies that chlorine dioxide would not be released through disproportionation in the Matsumoto system.

Finally, if any chlorine dioxide were generated, it would immediately react with Fe or Fe^{+2} because of the very high oxidation potential of chlorine dioxide:



Therefore, the system utilized by Matsumoto would not produce chlorine dioxide and, in any case, would consume any that was produced. In addition nowhere does Matsumoto mention the use of electromagnetic energy (light, e.g.) to produce chlorine dioxide gas.

¹ Masschelein WJ, "Chlorine dioxide: Chemistry and Environmental impact of oxychlorine compounds", Ann Arbor Science, Ann Arbor, Michigan, 1979, p 45 (copy attached hereto).

BTEC 9643
PATENT

7. U.S. Patent No. 5,330,661 to Okuda teaches a process and apparatus for treating water contaminated with a toxic organochlorine solvent. More specifically, Okuda describes decomposition of organochlorine solvents to form carbon dioxide, water, hydrochloric acid, etc. (column 3, lines 40 to 47) by UV irradiation of an aqueous system containing barium titanate and dissolved hydrogen peroxide and/or ozone. Ozone is added to the reaction system before organochlorine decomposition and is not generated by reaction. Carbon dioxide is generated by the decomposition of organic matter, not by the oxidation or reaction of anions to generate a gas. Such decomposition reactions were addressed by applicants in the background of the subject application at page 1, lines 20 to 29, wherein it is stated that "[c]arbon dioxide is generated by the decomposition of organic matter, not by the oxidation of anions." Okuda therefore does not describe the reaction of anions to generate and release a gas as claimed.

8. U.S. Patent No. 5,008,096 to Ringo teaches a method for enhancing generation of chlorine dioxide by contacting an aqueous medium containing a dissolved chlorine dioxide precursor (e.g., sodium chlorite) with an amount of chlorine gas, sodium hypochlorite, or hydrochloric acid which reacts with a catalytic amount of a transition metal. Chlorine dioxide is said to be generated in response to increased acidity (column 3, lines 6 to 8 and column 4, lines 3-17). Chlorine dioxide is described as being generated from dissolved sodium chlorite in acidic systems in the absence of a transition metal (column 3, lines 56 to 63, and throughout the Examples). Thus, chlorine generation does not result from an electromagnetic energy mechanism. A transition metal is described only as a gas generation enhancer (column 3, line 64 to column 4, line 2, and throughout the Examples). Generation and release of a gas through activation of a catalyst with electromagnetic energy and reaction with an anion is not described or suggested. Ringo therefore does not describe the reaction of anions to generate and release a gas as claimed.

9. U.S. Patent No. 5,753,106 to Schenck teaches a method of oxidative purification of a medium that contains contaminants in the form of an oxidizable carbon compound. Example 5 describes decomposing by UV irradiation trichloroethane solvent in an acidic aqueous solution containing dissolved sodium persulfate. The contaminants are decomposed

BTEC 9643
PATENT

according to a series of reactions as described at columns 2 to 3 of the patent. Column 14, lines 33-56 describes adding hydrogen peroxide and titanium dioxide as decomposition enhancers. As with Okuda, a gas is generated by the decomposition of organic matter in the absence of a catalyst, not by the oxidation or reaction of anions to generate a gas. Schenck therefore does not describe the reaction of anions to generate and release a gas as claimed.

10. U.S. Patent No. 5,772,897 to Hancock teaches a catalytic oxidation process in an aqueous medium comprising adding an oxidizing agent to the aqueous medium and passing the mixture through a fixed bed of a particulate catalyst. The oxidizing agent is decomposed by the catalyst with the evolution of oxygen (column 2, lines 18 to 29). Nowhere in Hancock is the catalyst described as being "capable of being activated by electromagnetic energy," or "capable of being activated by light" as required in the present claims. Therefore, the claims are not anticipated by Hancock because Hancock does not teach energy activated oxidation, anions capable of generating a gas, a gas-releasing composition or reaction of anions to generate and release a gas. Hancock teaches decomposition to form carbon dioxide and water (column 3, lines 20-32 and Example 4) by the decomposition of organic matter, not by the oxidation of anions (column 5, line 35; Example 4; application specification at page 1, lines 20-29).

11. In fact, Hancock teaches the minimization of gas evolution (column 1, lines 56 - 59; column 4, lines 1-5) and therefore teaches away from the present invention. Hancock goes on to teach that leaching of the catalyst into the effluent is undesirable (column 4, lines 6-11). Nowhere does Hancock describe anions capable of generating a gas, a composition comprising the catalyst and solid or solid containing suspension containing the anions, or a gas releasing composition. If the anions in Hancock were energy activated, as in the present claims, then the peroxide would form ozone, not oxygen, and the hypochlorite would form chlorine, not oxygen.

12. U.S. Patent No. 6,306,352 to Yoshida teaches an oxygen-generating material which is prepared by packaging solid peroxide and peroxide decomposition catalyst in a moisture-permeable material. The oxygen generating materials of Yoshida generate oxygen by coming in contact with water or moisture (column 8, lines 6 to column 9, line 6). Like Hancock, Yoshida describes moisture activated decomposition, not energy activated oxidation or reaction of anions, to generate and release a gas. Yoshida also includes a moisture-activated decomposition catalyst to catalyze the decomposition of hydrogen peroxide into water and

BTEC 9643
PATENT

oxygen gas. If the decomposition in Yoshida were instead energy activated, as in the present claims, then Yoshida's composition would produce ozone, not oxygen. The fact that the decomposition described by Yoshida would produce ozone if it were energy activated, shows that Yoshida does not teach or suggest the possibility of energy activation.

13. U.S. Patent No. 5,783,105 to Zhang teaches a breathable oxygen gas generation composition comprising substantially carbon-free tin as fuel and rheological modifier, a transition metal oxide as catalyst and an oxygen source consisting of alkali metal chlorates or perchlorates. The oxidation of the gas-producing anions is thermally activated through the ignition and combustion of tin (column 5, line 65 through column 6, line 8). An ignition pellet is ignited by firing a percussion primer which then initiates tin combustion that thermally catalyzes the oxidation of the oxygen source thereby releasing oxygen gas. Such use of metal oxides as thermally activated catalysts for the oxidation of inorganic anions provide uncontrolled, irreversible, rapid and voluminous oxygen gas release for use in aircraft oxygen generators. Zhang does not describe the use of the transition metal catalysts as electromagnetic- or photo-catalysts to initiate controlled generation and release of a gas. Zhang does not teach, suggest, or provide any motivation to generate a gas from an anion through electromagnetic energy-activated catalysis as claimed in the present invention. No disclosure in Zhang would have motivated the skilled person to make the energy-activated compositions of the claimed invention.

14. U.S. Patent No. 5,896,126 to Yoshida teaches an air bag gas-generating composition comprising an azodicarbonamide, an oxo halogen acid salt and a nitrate. The gas generation mechanism involves the thermal activated oxidation of an organic compound containing nitrogen by an oxo halogen salt or nitrate to provide gas release for use in automotive air bags (column 3, lines 6-27). An igniter is electrically detonated to thermally oxidize the organic compound thereby releasing nitrogen gas. Addition of metal oxide is taught as a combustion control catalyst to adjust burning velocity (column 5, lines 30-45). Although Yoshida's composition may include a metal oxide, it serves as a combustion control catalyst and does not catalyze oxidation or reaction of anions to generate and release a gas, as in the claimed invention (column 5, line 30 to column 6, line 36). The function of the metal oxide in Yoshida's composition is to control the burning velocity within acceptable limits, not to catalyze the oxidation reaction.

BTEC 9643
PATENT

15. Yoshida, U.S. '126, does not teach, suggest, or provide any motivation to generate a gas from an anion through electromagnetic energy-activated catalysis as claimed in the present invention. Yoshida's description of thermal activated oxidation of an organic compound containing nitrogen by an oxo halogen salt or nitrate to provide uncontrolled, irreversible, rapid and voluminous nitrogen gas release for use in automotive air bags would not have motivated one skilled in the art to make the claimed invention, and would not have provided any guidance as to how to do so. The use of chlorite or hypochlorite would not have resulted in oxidation or reaction of such anions to generate and release chlorine dioxide or chlorine gas as suggested by the Office. Therefore, even if one was motivated from Yoshida's disclosure to select and substitute applicant's claimed anions, the substitution does not result in the claimed invention.

16. U.S. Patent No. 5,411,643 to Cawfield teaches a process for producing manganese dioxide and zinc metal by using chloric acid to separate zinc oxide and manganese oxide. In Cawfield, manganese oxide is reacted with a molar excess of chloric acid to form chlorine gas, a solid phase containing manganese dioxide, a liquid phase containing chloric acid and water. The chloric acid dissociates into hydrogen ions and chlorate ions in aqueous solution. If the chlorine gas resulted from energy activation of anions, as required by the pending claims, then the result would be hypochlorite, not chlorate anions as in Cawfield.

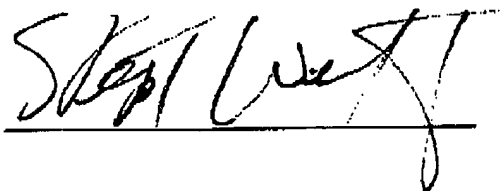
17. The purpose of the process taught in Cawfield is to produce manganese dioxide and zinc metal. Nowhere does Cawfield teach, suggest, or provide any motivation to generate a gas from an anion through electromagnetic energy-activate catalysis as claimed in the present invention. While Cawfield may include a metal oxide, the purpose of his invention is to separate the zinc oxide and the manganese oxide to produce manganese dioxide and elemental zinc. The metal oxide in Cawfield does not serve to catalyze oxidation or reaction of anions to generate and release a gas as in the claimed invention. The function of the metal oxide in Cawfield is to serve as the basis for the production of an elemental metal, not to catalyze the oxidation reaction.

18. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the

BTEC 9643
PATENT

Unites States Code, and that such willful false statements may jeopardize the validity of the
above-referenced

Date: 20 March 2006

A handwritten signature in black ink, appearing to read "Stephen West", written over a horizontal line.

CHLORINE DIOXIDE

Chemistry and Environmental Impact of Oxychlorine Compounds

by

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CHAPTER 10

REDOX REACTIONS OF CHLORINE
DIOXIDE AND CHLORITE

OXIDATION CAPACITY AND POWER

The literature gives the following redox potentials (25°C):

- | | | |
|---|-----|----------|
| $\text{HClO}_2 + 3 \text{H}^+ + 4\text{e}^- = \text{Cl}^- + 2 \text{H}_2\text{O}$ | (1) | : 1.57 V |
| $\text{HOCl} + \text{H}^+ + 2\text{e}^- = \text{Cl}^- + \text{H}_2\text{O}$ | (2) | : 1.49 V |
| $\text{Cl}_2 + 2\text{e}^- = 2 \text{Cl}^-$ | (3) | : 1.36 V |
| $\text{ClO}_2 + \text{e}^- = \text{ClO}_2^-$ | (4) | : 0.95 V |
| $\text{ClO}_2^- + 2 \text{H}_2\text{O} + 2\text{e}^- = \text{Cl}^- + 2 \text{OH}^-$ | (5) | : 0.9 V |
| $\text{ClO}_2^- + 2 \text{H}_2\text{O} + 4\text{e}^- = \text{Cl}^- + 4 \text{OH}^-$ | (6) | : 0.78 V |

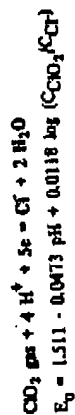
The $\text{ClO}_2 + 5\text{e}^- = \text{Cl}^- + 2 \text{OH}^-$ reaction is an unknown redox couple. The potential of couple 4 cited above depends on the temperature between 5 and 35°C as is given below:

$$E_{\text{ClO}_2/\text{ClO}_2^-} = (-5.367 + 0.0613 T - 19.4 \times 10^{-5} T^2 + 3 \times 10^{-7} T^3) \text{volts}$$

In aqueous solution, it decreases linearly as a function of the pH with a coefficient of -0.062 and that by the unit increase of pH. The oxidation-reduction potential according to reaction 1 depends on the pH according to:

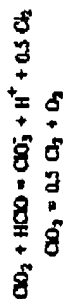
$$E_0 = 1.57 - 0.0443 \text{ pH} + 0.0148 \log (\text{ClHClO}_2/\text{Cl}^-)$$

The complete reduction of ClO_2 in acid medium evolves according to:



46 CHLORINE DIOXIDE

It seems that hypochlorous acid is a stronger oxidant than is chlorine dioxide in aqueous solution. Consequently one may observe the following reactions (1):



The kinetic equation becomes:

$$\frac{d[\text{ClO}_2]}{dt} = K_1 [\text{ClO}_2] [\text{HClO}] + K_2 [\text{ClO}_2]$$

where $K_1 = 1.28$ and $K_2 = 0.022$ at 25°C .

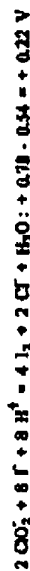
In the presence of chlorine dioxide, chlorine reacts selectively with ICl_3 forming ICl_3 (2). With bromine, which has a redox potential of 1.14 V, the experimental equilibrium is (3):



The reaction tendencies between iodide, chlorine dioxide and chlorine are (E° , V ; I_2 : + 0.54 V):



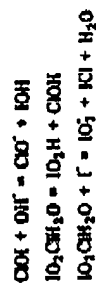
The reaction is carried out quantitatively in neutral or acid solutions as well as in CCl_4 :



In this case, iodides are quickly oxidized at pH below 4. The oxidizing agent is probably nascent chlorous acid:



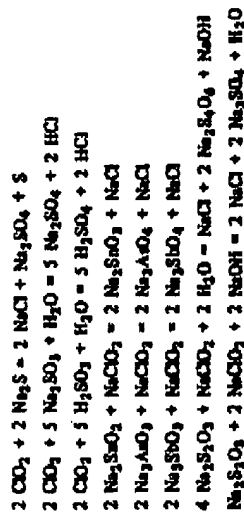
In neutral solution, the reaction is very slow: 50% of the oxidation with chlorine is attained after 70 hours (4). The same phenomenon takes place at the second stage of oxidation with chlorine dioxide. As the mechanism of the reaction is very complex, the determining step would be (5):



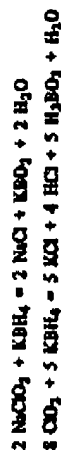
From the tables of redox potential, one may easily deduce thermodynamically possible oxidations involving chlorine dioxide or chlorine in aqueous solution. Here will be treated only the reactions which were effectively

REDOX REACTIONS OF CHLORINE DIOXIDE AND CHLORITE 47

considered. A number of reactions lead to the exploiting of a maximum oxidation capacity of ClO_2 . In these conditions chlorite reacts by 4 equivalents. Where analytical applications are concerned, it is generally preferable to carry them out in acid media.

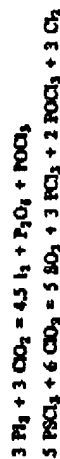


Potassium borohydride enables the following reductions without interference of chlorite (6):



With chlorite, the oxidation of BH_4^- is catalyzed on copper surfaces at pH values at least as high as 11.8 to 13.6 (7).

In an anhydrous medium the derivatives of trivalent phosphorus are often oxidized to compounds of pentavalent phosphorus (8):



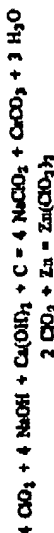
Oxychloride and pentachloride are formed from phosphorus trichloride. In CCl_4 , 5 moles of phosphorus trichloride react with 2 moles of ClO_2 forming a mixture of POBr_3 and solvated pentachloride ($\text{PBr}_5 \cdot 2\text{CCl}_4$) (8).

Among the phosphorus esters, $\text{HO}(\text{OR})_2$ is inert to chlorite, while $\text{P}(\text{OR})_3$ is quickly oxidized (9). Sulfur trioxide reacts with KClO_2 forming Cl_2O and $(\text{ClO}_2)_2\text{S}_2\text{O}_5$. With chlorine dioxide, an unstable derivative is formed, $\text{Cl}_2\text{O}_2 \cdot \text{nSO}_3$, which through rapid decomposition forms $(\text{ClO}_2)_2\text{S}_2\text{O}_5$ (10).

Simple cyanides and cyanides complexed with copper are oxidized with ClO_2 :



REDOX REACTIONS OF CHLORINE DIOXIDE AND CHLORITE 49



This latter reaction is, from the historical point of view, one of the very first industrial syntheses of chlorite. With the technical grade of Zn (84%) the particle size must be less than 0.15 mm. The $\text{Zn(ClO}_2)_2$ is converted to NaClO_2 with NaOH , Na_2CO_3 or NaHCO_3 . With carbonates the conversion is unsatisfactory while with NaOH the disproportionation to chlorites and chlorates must be emphasized; with a Zn concentration of 34.6 g/l the conversion to 0.52 M NaClO_2 is 70 mole % with the impurities CO_2 (10) and Cl^- (20 mole %). With NaHCO_3 the concentration of Zn was 231.3 g/l and the product 4 M NaClO_2 without significant disproportionation.

A certain number of oxidants result in the formation of chlorine dioxide from chlorites (15):



According to experiences carried out with radioactive tracer molecules, the chlorine atom of the dioxide originates from the initial chlorite (16). The side reaction of the corresponding anions is:



depending on the pH of the medium. Cations accelerate the reaction in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+ < \text{Rb}^+ < \text{Ba}^{++}$. Anions inhibit the reaction in the order of increasing negative charge (17):



On the other hand:



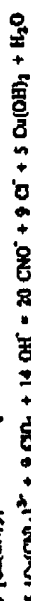
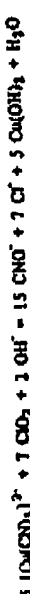
Chlorine dioxide is oxidized with Co(III) ions in 0.3 to 2 M perchloric acid solutions according to (18): $\text{Co(III)} + \text{Cl}^- = \text{Co(II)} + \text{Cl(V)}$.

DISPROPORTIONATIONS

The chlorite ion is unstable at low pH values, < 2 , and decomposes according to the overall stoichiometry:

48 CHLORINE DIOXIDE

The reaction is instantaneous with the ratio $\text{ClO}_2/\text{CN}^- > 5.2$ (11). Complexed cyanides react according to:



The necessary ratio is $\text{ClO}_2/\text{CN}^- = 1.2$. This reaction evolves in two stages: first attack of simple as well as complexed cyanides by ClO_2 to form CNO^- and subsequent catalyzed oxidation of complex cyanides by CNO^- which is reduced to Cl^- . At a copper concentration of 25 mg/l the oxidations are reported to be complete within 10 minutes. Simple cyanides are not oxidized by chlorite.

The oxidations with chlorine dioxide often lead to chlorites. Normally, these reactions may be applied to the industrial synthesis of sodium chlorite:



However, chlorites may react with hydrogen peroxide:



The two stages are bimolecular. The velocity of the former is $4 \times 10^{-4} \text{ l-mole}^{-1} \text{ min}^{-1}$ with an activation energy at 80°C of 20.4 kcal/mole and a temperature coefficient of 2.8. The velocity of the second stage which is considerably higher could not be measured (12).

According to Høst (13), reduction of a redox potential below -0.2 V generally form chlorides. The metallic compounds of a potential higher than +0.5 V cause catalytic disproportionations of chlorite (vide *infra*).

Let us also note the moderated reduction of chlorine dioxide to sodium chlorite by sulfurous anhydride and the possibilities of perborate and ammonite for this reduction (14):



One can carry out reductions in a heterogeneous system such as:

REDOX REACTIONS OF CHLORINE DIOXIDE AND CHLORITE 51

$$\frac{d[\text{ClO}_2]}{dt} = (5 \times 10^3 \exp(-7.350/T) + 1.67 \times 10^8 \exp(-7.350/T) \times [\text{OH}^-] [\text{ClO}_2]) + (2.67 \times 10^8 \exp(-7.350/T) + 7.37 \times 10^8 \exp(-3.875/T) [\text{OH}^-]) [\text{ClO}_2]^2$$

According to this approach, the half-life of chlorine dioxide at pH 12 and an initial concentration of 5 to 10 mg ClO₂/l is about 3 hours.

Under certain conditions, one may obtain a specificity in relation to the cation used for the disproportionation (22):



Another alkaline disproportionation of ClO₂ is the following (23):



Other disproportionations may occur in neutral media such as:



Sodium chlorite may disproportionate according to the reaction:



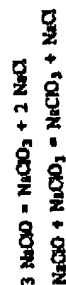
The latter, which is common to alkaline chlorites and alkaline earth chlorites may be obtained by heating at 180° to 210°C. For chlorous acid, the reaction is similar (24):



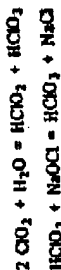
In the dark, the reaction is very slow: 3.4% HClO₂ is formed after 24 hours. The disproportionation reactions of chlorine dioxide quicken when mixtures containing hypochlorite are treated. One must consider the oxidation reaction commented on earlier:



In addition, there are disproportionations of hypochlorites and mixed disproportionations of hypochlorites and chlorites:



In the presence of chlorine dioxide, the following equations are proposed:



50 CHLORINE DIOXIDE



The disproportionation reactions are particular cases of oxidation-reduction reactions. In the case of chlorine dioxide the disproportionations are very important for stability. Chlorine dioxide pure and in aqueous neutral solutions is really much more stable than has sometimes been described. Also, half of the chlorine dioxide is oxidized and is lost in certain applications as, for example, pulp bleaching. The reaction is described by the net equation:

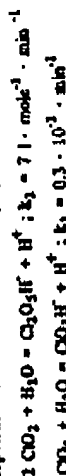


However, in order to proceed, the reaction needs alkalinity. In basic aqueous solutions it undergoes an irreversible disproportionation:



The reaction is only total when the pH is above 11. UV radiation exists the disproportionation of aqueous chlorine dioxide, the main products being: O₂, Cl⁻ and ClO₂⁻, and the reaction is more rapid in an alkaline medium (19).

Although it appears simple, this case is very complex from the mechanism and reaction kinetics viewpoints. The reaction would also initially comprise a bimolecular step and a monomolecular step, the relative importance of which depends on the concentration (20):



If the OH⁻ concentration is maintained constant, the overall reaction is the sum of the two reactions. The bimolecular step is dominating at the beginning and the monomolecular step at the end. The kinetics as a whole has been the subject of a very elaborate study of the function of alkali. The conclusions are the following (21):

$$\frac{d[\text{ClO}_2]}{dt} = k_1[\text{ClO}_2] + k_2[\text{ClO}_2]^2$$

$$k_2 = (3 \times 10^7 + 10^{10} [\text{OH}^-]) \exp(-14,600/RT) + 1.3 \times 10^7 [\text{ClO}_2] \exp(-24,800/RT)$$

$$k_1 = 1.6 \times 10^{13} \exp(-14,600/RT) + (4.4 \times 10^8 [\text{OH}^-] + 1.3 \times 10^8 [\text{ClO}_2]) \exp(-7,700/RT)$$

In another approach in which the carbonate alkalinity is neglected, the following equation is formulated:

52 CHLORINE DIOXIDE



The initial presence of chlorite favors these reactions. A typical example of the complexity of the disproportionation reactions of chlorine dioxide is given in Figure 10.1. The initial concentration of ClO_2 is 103 mg/l at pH 8.4.

NaClO_2 : A, -, B, -, C, -, D, -, E, -, F, -, G, 123, H, 123, I, 123, J, 123, K, 123, L, 62

NaClO : A, -, B, 103, C, 132, D, 244, E, 348, F, 440, G, -, H, 27, I, 79, J, 165, K, 161, L, 161

Hypochlorite has been known to cause ClO_2 losses in moderately basic media. Chlorite has only little direct influence. On the other hand, in the presence of NaClO , it speeds up the reaction which leads to ClO_2 losses. More recently it has been reported also that the losses of ClO_2 as a result of chlorate formation during bleaching are usually 20 to 30%. The addition of chlorite to the ClO_2 bleaching mixture enhances the formation of chlorite (25).

Experiments with radioactive tracer molecules have shown fast exchange: $\text{Cl}^{36}\text{O}_2 + \text{ClO}_2 = \text{ClO}_2 + \text{Cl}^{36}\text{O}_2$ (26). In the alkaline disproportionation of chlorine dioxide, the formed chlorite has an identical composition to that of the starting dioxide. No exchange is observed between chlorine dioxide and ClO_2 , ClO_2 , Cl_2 , Cl^- , while there exists a slow exchange between chlorine dioxide and hypochlorous acid (27).

In practice, all these observations have a certain importance. The stability of chlorine dioxide in aqueous solution is influenced by its purities. Besides, the eventual presence of alkaline hypochlorite plays a very important role. On the other hand, the elimination of chlorine dioxide from a ternary mixture ClO_2 - Cl_2 - NaClO_2 by alkaline disproportionation is a technique with a doubtful analytical application (see Chapter 12). Finally, studies carried out on the reactivity of chlorine dioxide, and based on the consumption of the latter, are to be calculated according to the stability of ClO_2 in experimental conditions.

53 REDOX REACTIONS OF CHLORINE DIOXIDE AND CHLORITE 53

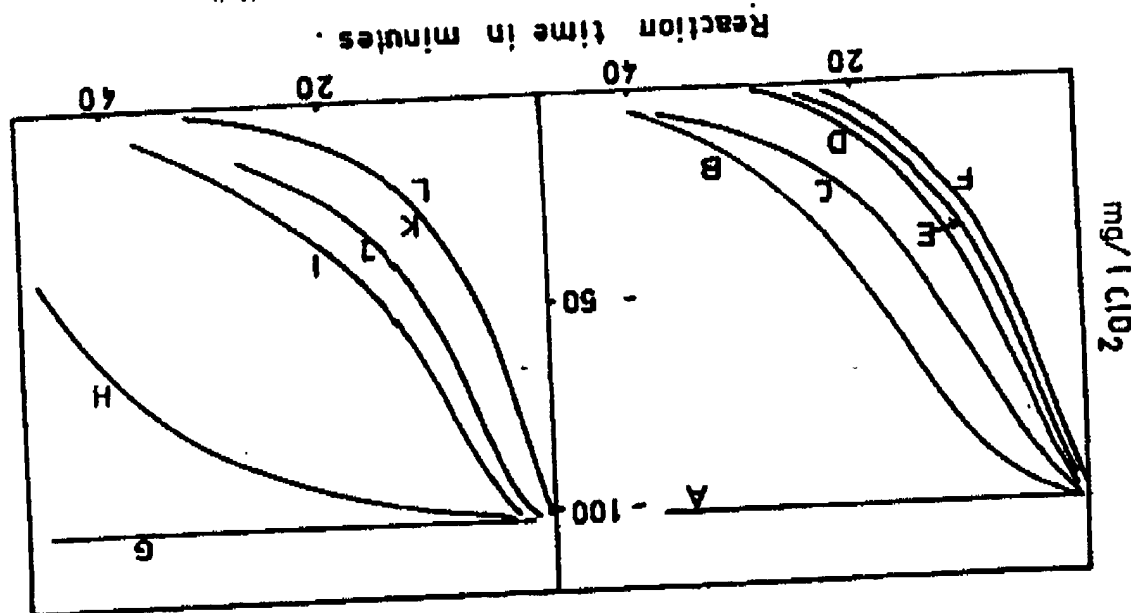


Figure 10.1 The decomposition of ClO_2 in the presence of chlorite and hypochlorite.

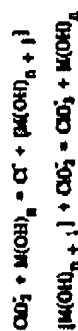
54 CHLORINE DIOXIDE

OXIDATION OF METALLIC SALTS BY CHLORITE
AND CATALYTIC DISPROPORTIONATION OF CHLORITES

Salts of bivalent ferrous ion and manganese are oxidized quantitatively by sodium chlorite in an alkaline medium. Trivalent chromium salts $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_2$, $2\text{Cr}_2\text{O}_3$, $3\text{H}_2\text{O}$ and Cr_2O_3 are oxidized at temperatures up to 80°C in chromate by aqueous sodium chlorite (28). On the other hand (29):

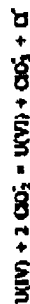


In alkaline media, other hydroxides oxidizable by chlorite react similarly; however, the reactions often are only partial. Catalytic disproportionations of chlorite also are observed. The general principle of these disproportionations would be (30):



The catalytic action varies as a function of the metal and according to the sequence $\text{Ni} \gg \text{Co} > \text{Cu} > \text{Fe}$. The mixing of several hydroxides increases the speed of catalytic disproportionation. Where alkaline earth chlorites are concerned, there exists an effect of the chlorite cation. With $\text{Ni}(\text{OH})_2$: $\text{Ba} < \text{Ca} < \text{Sr}$; and with hydroxides of Fe, Cu and Co: $\text{Ba} < \text{Sr} < \text{Ca}$. These catalytic disproportionations take place within a limit of pH 8 to 12.

Tetravalent uranium salts are oxidized by chlorine dioxide and acid sodium chlorite (31, 32). A transfer of O_2 from the oxidizing agent to the uranium salts may be observed. The stoichiometry of the reaction varies slightly and has some connection with the catalytic disproportionation:



Indeed there exists an initial favorable proportion of $\text{ClO}_2/\text{U(VI)}$ of two. It decreases to 1 in the presence of phenol, which eliminates the intermediate ClO gradually during its formation.

In a highly acid medium, chlorine dioxide is formed rapidly, oxidizing the U(VI) salts to U(VI) ; simultaneously, there is disproportionation between chlorides and chlorates. Chloric acid operates the same oxidation

REDOX REACTIONS OF CHLORINE DIOXIDE AND CHLORITE 55

slowly, and the final result is as if there had been intervention of the two electrons oxidizing initial chlorite (33).

OXIDATION OF METALS—
CORROSION BY CHLORINE DIOXIDE AND CHLORITES

Most metals in the powdered state are oxidized by chlorine dioxide (34). By the action of ClO_2 (65 g/l) on pulverized metal (45 g/l) one obtains the following corresponding chlorites and yields: Cd: 66%; Zn: 57%; Mg: 64%; Al: 34%.

Nickel chlorite formed under similar conditions undergoes a rapid disproportionation into chlorides and chlorates. For powdered iron one obtains a slow reaction; on the contrary, powdered iron in a solution of copper sulfate makes chlorine dioxide react very quickly. There is a deposit of copper on the iron and an accelerated dissolution of the latter. These phenomena follow the tendency expressed by the normal potential of iron and copper. These reactions are very important in the case of the simultaneous treatment of swimming pool water by chlorine dioxide and copper sulfate (35).

In reactors, lead resists corrosion by chlorine dioxide. Aluminum, pre-oxidized or connected to an anodic protection, resists contact with chlorine dioxide. Alloys of aluminum such as corrosion resistant F32 and perlanus 30 resist solutions of ClO_2 or NaClO_2 . Alloys of silver containing 2 to 7% Cd or Zn, or 1 to 3% Pb resist satisfactorily. An alloy based on nickel and resisting bleaching conditions by acidified chlorite contains: Cr: 10-28; W: 0-10; Mn: 0-2; C: 0-1; Si: 0-1; Ni: 40; Fe: 4-5; and Mo: 4-5% (36).

Titanium is used to a great extent owing to its good resistance to chlorine dioxide. Durichlor has good resistance to ClO_2 , but is limited by its mechanical properties. Hastelloy C and Chlorimet 3 are very satisfactory. Duricon a little less. Bour R 55 does not resist condensed ClO_2 . Monel, Inconel, broze and ferritic stainless steels are not suitable for ClO_2 bleaching (37). Titanium is resistant to 5% HCl at room temperature but only to 0.5% at 100° . The stability in 30 to 40% H_2SO_4 at 40°C is improved by ClO_2 . In a general way it is recommended to use a Ti-Pd alloy containing 0.2% Pd (38, 39).

On the other hand, titanium may be used for anodic protection against corrosion by chlorite in solution. The titanium anode is connected to the positive pole from an external source and the negative pole is attached to the apparatus. The current density is at least 0.3 amp/C/m^2 ; C being the concentration in g NaClO_2/l (40).

REDOX REACTIONS OF CHLORINE DIOXIDE AND CHLORITE 57

Finally, chlorine dioxide treated in a cooled solution of CCl_4 by pyridine or its homologs produces a reaction product of unknown composition (52).

Chlorite and chlorine dioxide in neutral aqueous solutions form a bimolecular association complex $[\text{ClO}_2 \cdot \text{ClO}_2]^-$ represented as Cl_2O_4 . The absorption of the complex at 270 mμ is not significantly different from that of the chlorite ion. The formation constant (1.5 M^{-1}) can be measured at 360 mμ. The extinction coefficient of the complex is 90 to 100 $\text{mole}^{-1} \text{ cm}^{-1}$ compared to that of ClO_2 , 1,240 $\text{mole}^{-1} \text{ cm}^{-1}$.

The Cl_2O_4 dimer is also considered as a hypothetical intermediate in the potentiometric titration of chlorite with chlorine dioxide in dimethyl sulfoxide (53).

Chlorine trioxide reacts with an excess of AlCl_3 to produce $\text{Al}(\text{ClO}_2)_3$, while if the oxide is in excess, four moles of Cl_2O_4 are consumed per mole of AlCl_3 . Reaction products are $\text{Al}(\text{ClO}_2)_3$, ClO_2 and Cl_2 (54).

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56 CHLORINE DIOXIDE

More details on the corrosion of various steels can be found in specialized literature (41, 42, 43).

Another method of protection is the selective attack of an aluminum electrode. This technique consumes the electrons available for oxidative corrosion by a material (aluminum) which kinetically reacts faster than the structure to be protected. Its success is variable.

Metal corrosion by aqueous solutions of sodium chlorite may be diminished by adding certain salts, such as nitrates, phosphates, disodium phosphate or sodium pyrophosphate.

Certain commercial chlorites contain these additives. One can also fight corrosion with 0.5-4 g/l of acid or neutral tartrates of Na, K or NH_4 , or even organic amino compounds such as amines, amides or heterocyclic bases (44). Oxalate and fluorides promote corrosion, as do inorganic ingredients of deicers (45). The attack of stainless steel by chlorine dioxide may be avoided by adding small amounts of nitric acid or saturated C_1 to C_4 aliphatic acids to the vapor (46). Wood undergoes a slow delignification when ClO_2 is present. Sandstone, ceramic glass and asbestos cement are perfectly resistant. Polyurethanes, polymethacrylates and their copolymers resist solutions of ClO_2 and NaClO_2 (47), as well as ketones and polyvinyl chloride. Coatings resistant to ClO_2 are nitro polymers of polystyrene and natural rubber (48). The use of polyamides is not indicated.

THE FORMATION OF COMPLEXES

Coordination complexes of the chlorite ion of the following type:

$\text{M}_2^{\text{II}}, \text{M}_2^{\text{III}}, \text{M}_2^{\text{IV}}(\text{ClO}_2)_2$, where $\text{M}^{\text{I}} = \text{K}, \text{Rb}, \text{Cs}$ or NH_4 ; $\text{M}^{\text{II}}, \text{Cu}$ or Cd and $\text{X} = \text{Cl}, \text{Br}$ or I (49) are known and are obtained by mixing

a metallic salt such as CdCl_2 in alcoholic solution with the chlorite of the monovalent metal. Attempts to prepare complexes of the same type have been carried out with zinc or mercury and have failed.

Another type of complex is: $[(\text{ClO}_2)_2\text{Co}(\text{NH}_3)_2]^{++}$, which is obtained by treating a cooled aqueous solution of $[(\text{Co}(\text{OH})(\text{NH}_3)_5)(\text{NO}_2)_2]\text{H}_2\text{O}$ with nascent chlorous acid. The complex is extracted from CCl_4 and precipitated by adding ethanol (50). Other complexes have the following composition:



and



where o-phen is orthophenanthroline. They are obtained by the oxidation of cobalt-o-phenanthroline complexes by sodium chlorite (51).

58 CHLORINE DIOXIDE

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